

THE PREPARATION OF *p*-NITROPHENYLMALEIC
ANHYDRIDE AND ITS APPLICATION TO THE
DIENE SYNTHESIS

BY

CHARLES JACKSON STRICKLER

B.S., Purdue University, 1942
M.S., University of Illinois, 1949

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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THE PREPARATION OF *p*-NITROPHENYLMALEIC ANHYDRIDE AND ITS APPLICATION TO THE DIENE SYNTHESIS

INTRODUCTION

The purpose of this investigation was to find a suitable method for the preparation of *p*-nitrophenylmaleic anhydride and to study its participation in the Diels-Alder diene reaction with particular emphasis on the directive effect of the nitro group on the reaction with unsymmetrical dienes.

DISCUSSION OF RESULTS

When *p*-nitrophenylsuccinic anhydride (1) was treated with N-bromosuccinimide in the presence of cumene hydroperoxide, *p*-nitrophenylmaleic anhydride could be isolated in 31-34% yield. The relative proportions of the reactants were critical; the yield fell sharply when other than the optimum proportions were used.

An alternate method for the preparation of *p*-nitrophenylmaleic anhydride by direct nitration of phenylmaleic anhydride (2) failed. Only *o*-nitrophenylmaleic anhydride was isolated.

That *p*-nitrophenylmaleic anhydride does participate in the Diels-Alder reaction as a *dienophile* has been demonstrated by its adduct formation with 1,3-butadiene, 2,3-dimethyl-1,3-butadiene, isoprene, 2-ethyl-1,3-butadiene, 2-isopropyl-1,3-butadiene, anthracene, and cyclopentadiene. In all cases, with both symmetrical and unsymmetrical dienes, one product was isolated. That the adducts with unsymmetrical dienes were 1-*p*-nitrophenyl-4-alkylcyclohex-4-ene-1,2-dicarboxylic acids was demonstrated by their degradation to the corresponding 1-phenyl-4-alkylcyclohex-4-ene-1,2-dicarboxylic acids (3). These results were predicted by the ionic transition state theory of the mechanism of the Diels-Alder reaction.

The dimethyl esters of these adducts (except that of anthracene) have been prepared using an ethereal solution of diazomethane.

That *p*-nitrophenylmaleic anhydride will participate in the Diels-Alder reaction as a *diene* has been demonstrated by its adduct formation with 1-vinylnaphthalene. This adduct has been proven to be a derivative of 1,1'-binaphthyl by degradation to 1,1'-binaphthyl. Physical methods of analysis also indicate this structure. If *p*-nitrophenylmaleic anhydride had participated in this reaction as a dienophile, the adduct would have been a derivative of either 1- or 2-phenylphenanthrene.

p-Methoxyphenylmaleic anhydride could not be prepared by the method used in this work. Two isomeric bromine-substituted *p*-methoxyphenylmaleic anhydrides were isolated; their structures were not determined.

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VITA

The author was born in Painesville, Ohio, on August 17, 1919. He attended the public schools of Geneva, Ohio, graduating from Geneva High School in June, 1937. In the fall of 1938 he entered Purdue University and received his Bachelor of Science degree in May, 1942. After eighteen months' employment at Abbott Laboratories, he entered the United States Navy in September, 1943. Upon discharge to inactive duty in October, 1947, he returned to Abbott until September, 1948. He then entered the Graduate College of the University of Illinois and received the degree of Master of Science in August, 1949.

